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Thermal processing of paper sludge and characterisation of its pyrolysis products

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ABSTRACT

Paper sludge is a waste product from the paper and pulp manufacturing industry that is generally disposed of in landfills. Pyrolysis of paper sludge can potentially provide an option for managing this waste by thermal conversion to higher calorific value fuels, bio-gas, bio-oils and charcoal. This work investigates the properties of paper sludge during pyrolysis and energy required to perform thermal conversion. The products of paper sludge pyrolysis were also investigated to determine their properties and potential energy value. The dominant volatile species of paper sludge pyrolysis at 10 °C/min were found to be CO and CO_2, contributing to almost 25% of the paper sludge dry weight loss at 500 °C. The hydrocarbons (CH_4, C_2H_4, C_2H_6) and hydrogen contributed to only 1% of the total weight loss. The bio-oils collected at 500 °C were primarily comprised of organic acids with the major contribution being linoleic acid, 2,4-decadienal acid and oleic acid. The high acidic content indicates that in order to convert the paper sludge bio-oil to bio-diesel or petrochemicals, further upgrading would be necessary. The charcoal produced at 500 °C had a calorific value of 13.3 MJ/kg.

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1. Introduction

Production of pulp and paper generates significant amounts of sludge waste, which is usually managed through landfilling. For each ton of paper production, the Australian paper industry generates close to 100 kg of waste that is disposed of in landfills (APPIC, 2005). Due to increased costs for landfill waste management, as well as increased public and government pressures to limit the waste to landfill disposal methods, the paper manufacturing industry is increasingly considering alternative waste management solutions. In a recent review, Monte et al. (2008) suggested waste minimisation should have the highest priority for the paper manufacturing industry. Re-use of paper sludge for cardboard manufacture was investigated by Taramian et al. (2007) who concluded that, although paper sludge has negative effect on cardboard strength, it may be possible for its fractional input in cardboard manufacture. Shin et al. (2005) investigated combustion as possible management route, which also enables energy recovery. Another potential waste management option for the paper sludge is through pyrolysis which produces bio-gas, bio-oil and charcoal products, all of which have potential viable applications.

The interest in pyrolysis of wastes and biomass materials has increased in recent years as it provides an option for thermal upgrading to higher calorific value fuels. Bio-oils produced from pyrolysis of wastes and biomass have been previously considered as sources of fuel for direct combustion (Stamatov et al., 2006) or feedstock for bio-diesel and chemical production (Yaman, 2004). Charcoal derived from biomass was traditionally used as metallurgical fuel, which has been recognised as a CO_2-neutral iron ore reductant (Rehder, 1994). Charcoal is also being considered as a soil amendment and fertiliser replacement (Lehmann et al., 2003), which enhances soil quality and provides an additional option for carbon sequestration. The bio-gas product of waste pyrolysis has a reasonable calorific energy, which can be combusted to provide the required internal heat of pyrolysis. While pyrolysis of a wide range of different biomass and waste materials has been investigated in the past, there is still limited data on pyrolysis of paper sludge waste and evaluation of its pyrolysis products.

The aim of this work is to thermally characterise the energy required to heat and pyrolyse paper sludge and to investigate the properties of the products of pyrolysis, bio-gas, bio-oil and charcoal. Quantification of these properties is important in the modelling of the pyrolysis process, as well as is determining the feasibility of the paper sludge management option through thermal upgrading.

2. Experimental

2.1. Paper sludge properties

Recycled paper sludge (RPS) was collected from a paper manufacturing industry located in Sydney that produces fine quality specialty papers. The properties of the recycled paper sludge sample are displayed in Table 1. On an air-dried basis, the moisture content of the sample was 8.5%; however, the amount of moisture on an as-received basis was significantly higher at 70% of the sample weight. This prompts the importance of the paper sludge

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Table 1
Analysis of air-dried paper sludge.

Proximate analysis (%)	
Moisture	8.5
Fixed carbon	23.7
Volatile matter	60
Ash	7.8
Ultimate analysis (%)	
Carbon	30.2
Hydrogen	4.32
Nitrogen	0.78
Sulphur	0.39
Calorific value (MJ/kg)	14.22

drying process for improvement of the overall energy efficiency of the pyrolysis process. The sample also contained 60% volatile matter and less than 24% fixed carbon on an air dry basis. The sample carbon content determined through ultimate analysis was found to be lower than in most biomass materials, which generally contain around 50% carbon (Strezov et al., 2003a).

2.2. Thermal analysis

The paper sludge sample used in this work was first dried in a vacuum oven for 4 h at 80 °C, after which it was subjected to thermal evaluation to determine its thermal behaviour during pyrolysis. The specific heat of the sample was determined using a Computer Aided Thermal Analysis technique. The apparatus used for this technique is shown in Fig. 1. It consists of an infrared furnace and arrangement of internals for heating of a packed bed of sample. The analysed sample weighing 1 g was packed to a density of 400 kg/m^3 in a silica glass tube. The packed sample was insulated on the sides with ceramics and heated under argon atmosphere with a constant flow of 5 ml/min. The heating rate of the furnace was fixed at 10 °C/min, and heating was carried out until the heating element reached 700 °C. Although commonly pyrolysis temperatures are limited to around 500–550 °C, the thermal analysis experiments in this work were conducted at higher temperatures to determine changes in the sample thermal behaviour, as well as to monitor the changes in energy balance.

Specific heat and thermal conductivity of the examined paper sludge were estimated simultaneously during continuous heating by applying an inverse numerical technique to the measured temperatures of the heating element and centre and surface temperatures of the sample. For the purpose of these calculations, the sample was divided into a grid with an assumed number of nodes across the radius. The heat balance for each node was calculated based on the heat conduction principle where heat accumulated by the node equals difference of input and output heats from the node. Estimated specific heat in this case had apparent values. During an endothermic heat effect, the specific heat showed increasing values, while during an exothermic reaction the specific heat values decreased. A more detailed description of the experimental procedure and technique evaluation using various calibration standards can be found elsewhere (Strezov et al., 2003b). In the current work, calculations for the specific heat and energy balance are generally based on the initial mass of the sample.

2.3. Gas and liquid chromatographic analysis

Volatiles evolved during pyrolysis of paper sludge were analysed separately using gas chromatography. A M200 micro gas chromatograph from MTI Analytical Instruments was connected to the gas outlet of the glass sample tube. A molecular sieve 5A column at 90 °C was used to separate H_2 and CO while analysis of CO_2, CH_4, C_2H_4, and C_2H_6 was performed on a Poraplot U column at 55 °C. Chromatograms were obtained every 85 s using a gas thermal conductivity detector. Helium gas at a rate of 50 ml/min was passed through 50 mg of sample while maintaining continuous heating rate of 10 °C/min up to the maximum heating temperature of 800 °C.

The bio-oils produced from pyrolysis of paper sludge at 500 °C were condensed at room temperature for further analysis. The bio-oils were first dissolved in dichloromethane and then analysed using a Shimadzu GCMS apparatus (Model QP2010), with a 30-m long SGE-BP1 column of 0.25-μm diameter. Prior to commencement with GCMS experiments the instrument was auto-calibrated using perfluorotributylamine (PFTBA).

3. Results

Fig. 2 shows the specific heat and thermal conductivity of the paper sludge during continuous heating at 10 °C/min. The specific heat at room temperature was measured at 0.8 MJ/m^3 K and started to increase with temperature showing a significant endothermic reaction with a peak at 120 °C. This reaction was most likely due to the release of strongly bonded water which remained stable in the sample after completion of drying. After this initial reaction and at temperatures above 200 °C, the specific heat was constant at 1.1 to 1.15 MJ/m^3 K. At 330 °C, the sample went through a second endothermic reaction followed by sharp exotherm, which was completed at 390 °C. This behaviour is typical for decomposition of cellulose, as shown previously by Strezov et al. (2003a). Thermal conductivity of the paper sludge under the prescribed experimental conditions was found to be approximately 0.2 W/mK at room temperature and after reaching 230 °C started to increase with temperature to 0.7 W/mK at 500 °C and 1 W/mK at 680 °C.

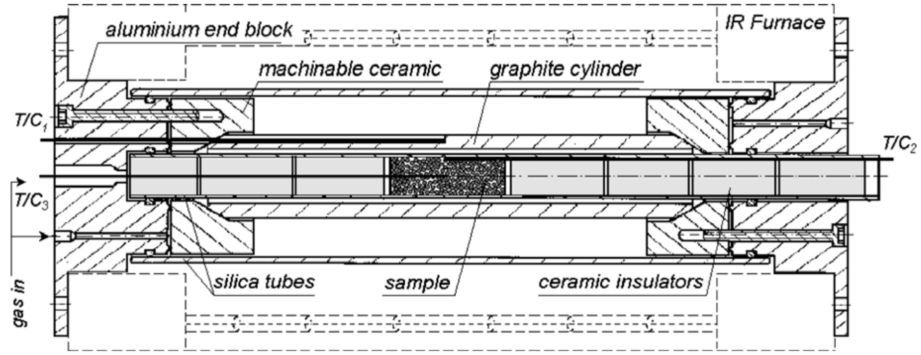

Fig. 1. Schematic diagram of the thermal pyrolysis apparatus.

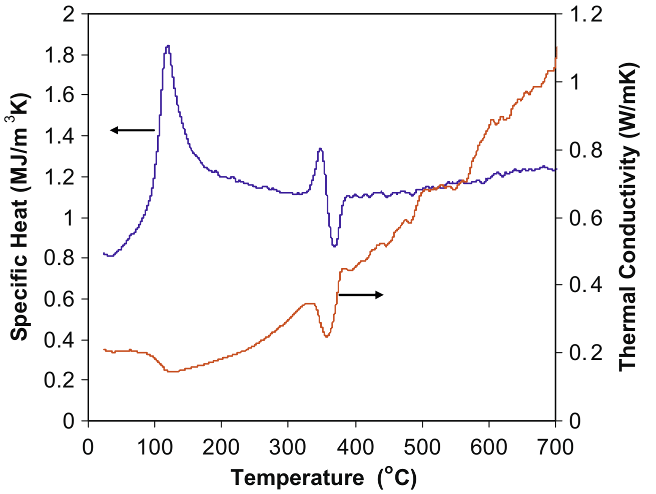

Fig. 2. Specific heat and thermal conductivity of paper sludge as a function of temperature.

Fig. 3 shows the evolution rate of volatile compounds with temperature expressed as percentage of the initial dry paper sludge sample weight. The most dominant volatile species in the off-gas was found to be CO_2. It started to evolve at temperatures as low as 80 °C, attributed to the release of occluded CO_2, but its evolution was mostly dominant above 200 °C. CO also started to evolve after 200 °C, and both CO_2 and CO reached their peaks at 340 °C corresponding to the endothermic peak shown in Fig. 2. The release of hydrocarbons occurred above 300 °C exhibiting peaks at 470 °C (C_2H_4 and C_2H_6) and 530 °C in case of CH_4. Hydrogen was released at temperatures above 470 °C.

With the measured specific heat and individual volatile species, it becomes possible to perform an energy balance of the paper sludge pyrolysis process under the current prescribed conditions. This information is used to determine the energy required to pyrolyse paper sludge and investigate the possible contribution of the bio-gas compounds to energy recovery into the pyrolysis system through internal combustion. For this purpose, a stoichiometric calorific value of the measured bio-gas species was calculated for each measured temperature. The calorific value was calculated as a sum of the heats of combustions of the individual gas compounds expressed on a weight basis. The energy required to heat the sample to a particular temperature was also calculated as a progressive integral of the measured apparent specific heat data from Fig. 2. An energy positive balance would mean that the heat of combustion of the evolved volatiles exceeds the energy required to heat the sample. For a dried paper sludge sample, the energy balance, shown in Fig. 4, becomes positive under stoichiometric and no-heat loss conditions only at temperatures above 500 °C. For torrefaction condi-

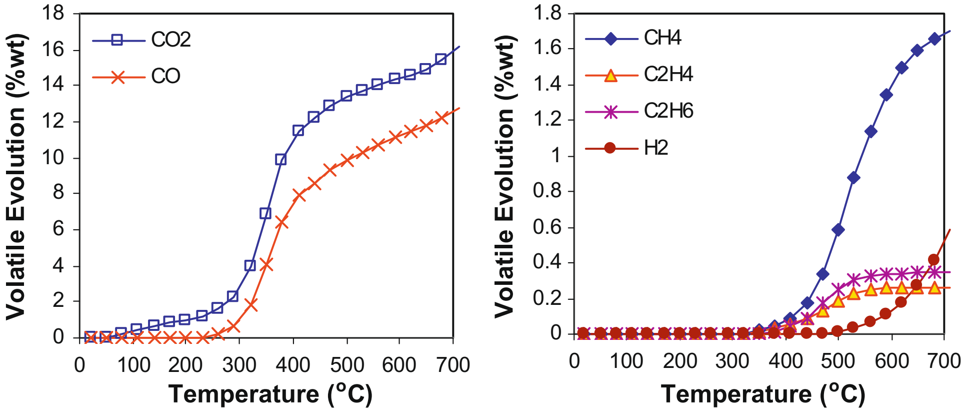

Fig. 3. Evolution of major volatile compounds during pyrolysis of paper sludge.

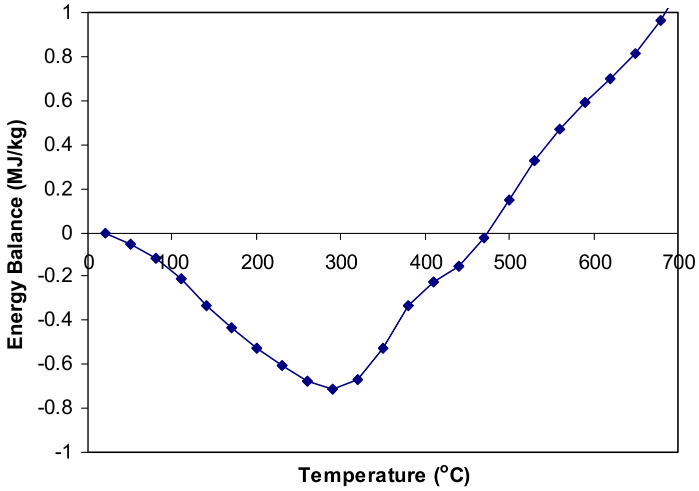

Fig. 4. Energy balance calculated as a difference between the calorific value of evolved volatiles and energy required to heat the sample to specific temperature.

Table 2
Yields of solid residue, bio-gas and liquid fraction with temperature.

T (°C)	Solid (wt.%)	Gas (wt.%)	Liquid (wt.%)
20	100	0	0
100	96	0	4
200	91	1	8
300	85	4	11
400	41	19	40
500	36	24	40
600	34	28	38
700	32	31	36

Table 3
Composition of bio-oil collected from paper sludge pyrolysis at 500 °C.

Number	Compound	Area (%)
1	Linoleic acid ($C_{18}H_{32}O_2$)	52.3
2	2,4-Decadienal ($C_{10}H_{16}O$)	21.5
3	Oleic acid ($C_{21}H_{40}O3$)	8.0
4	9-Octadecyne ($C_{18}H_{34}$)	3.0
5	1,3,7-Octatriene,3,7-dymethyl Ocimene ($C_{10}H_{16}$)	2.6
6	8-Heptadecene ($C_{17}H_{36}$)	2.2
7	4,8,12,16-Tetramethylheptadecan-4-olide ($C_{21}H_{40}O_2$)	1.2
8	Hexadecanoic acid ($C_{35}H_{68}O_5$)	1.1
9	Ethanol ($C_{20}H_{38}O_2$)	1.1
10	Kaur-16-ene ($C_{20}H_{32}$)	1.1
11	Hexadecanoic acid, ethyl ester ($C_{18}H_{36}O_2$)	0.8
12	2-Decenal, (E)-trans-2-Decenal ($C_{10}H_{18}O$)	0.5
13	9,12-Octadecadienoic acid, methyl ester ($C_{19}H_{34}O_2$)	0.5
14	Phenanthrene ($C_{20}H_{32}$)	0.5
15	Octadecanoic acid ($C_{39}H_{76}O_5$)	0.4
16	6,9-Octadecadienoic acid, methyl ester ($C_{19}H_{34}O_2$)	0.4
17	1-Indanone, 3,3,5,6,7-pentamethyl ($C_{14}H_{18}O$)	0.4
18	Tridecanedial ($C_{13}H_{24}O_2$)	0.4
19	1H-cyclopropa(a)naphthalene ($C_{15}H_{24}$)	0.3
20	Ethanone, 1,1′-(6-hydroxy-2-5-benzofurandiyl)bis-($C_{12}H_{10}O_4$)	0.3

tions (thermal upgrading at approximately 300 °C), the heat balance is overwhelmingly negative. For carbonisation conditions (thermal upgrading to 500 °C), the energy required to heat the dried sample to the temperature of 500 °C is estimated at 1.77 MJ/kg, while the calorific value of the pyrolysed bio-gas products is calculated at 1.5 MJ/kg. Although the energy balance is slightly net positive, when an industrial pyrolysis process is modelled, it is critical that the heat losses of the system, losses from the non-stoichiometric combustion conditions, and excess energy required to remove the free moisture should also be accounted for and carefully considered.

An additional parameter defining the quality of a thermal conversion process is the properties of condensed liquid products. The liquid pyrolysis products can be assumed to consist of two main components, the first comprising primarily water, while the second is the viscous bio-oils. The aqueous fraction is generally unwanted; however, it can still contain some amounts of viable chemicals, such as acetic acid and hydroxyacetone (Zhang et al., 2005). This fraction can be derived either from the occluded moisture present in the feedstock, or it can occur as a product of higher temperature dehydration reactions. Pyrolysis bio-oils are commercially desirable products. They are viscous tars containing predominantly oxygenated polar components which consist of aromatic and phenolic compounds (Sensoz, 2003). In this work, the total liquid fraction for the examined paper sludge was estimated by subtracting the total mass loss determined through thermogravimetric analysis and total bio-gas weight measured with micro gas chromatography. The variation in total solid, gas and liquid fractions with temperature is shown in Table 2. At 500 °C, the total charcoal produced was 36%, while the liquid fraction was estimated at 40% of the dried paper sludge weight.

The total liquid products evolved at 500 °C were further condensed at room temperature, dissolved in dichloromethane and analysed separately with a GC–MS instrument. The bio-oil analysis is shown in Fig. 5 and indicates a number of peaks detected in the GC spectra, all corresponding to individual chemical compounds. After background subtraction, identification of the chemical compounds was conducted using GCMS software's best fit match for the mass spectroscopic data and for each of the detected gas chromatographic peaks. The integral of each peak was used to approximate the relative concentration of each detected chemical compound. Table 3 summarises the list of compounds and corresponding percentage of the area obtained through integration of the GC–MS scan. Each compound number corresponds to the peak number from Fig. 5. The collected bio-oil was composed primarily of linoleic acid, also known as 9,12-octadecadienoic acid and a smaller fraction of 2,4-decadienal and oleic acid. The organic acids were the most dominant liquid species in the bio-oil fraction. Bio-oils are reportedly high in acids with their pH ranging between 2 and 3.7, which is considered as a significant disadvantage (Elliott, 2007; Oasmaa and Czernik, 1999; Yaman, 2004). Low bio-oil pH can often limit the application of this product as the oils can become corrosive to common construction materials. Hydrothermal processing is recommended to reduce the bio-oil acidity as well as to reduce the high oxygen content of the bio-oils. During this process bio-oils are upgraded to bio-diesel and marketable chemicals (Sanders et al., 2007).

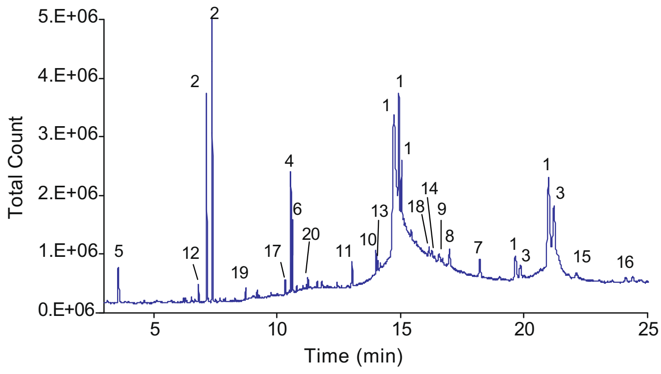

Fig. 5. Gas chromatographic analysis of bio-oils collected from paper sludge pyrolysis at 500 °C. Peak numbers correspond to compounds on Table 3.

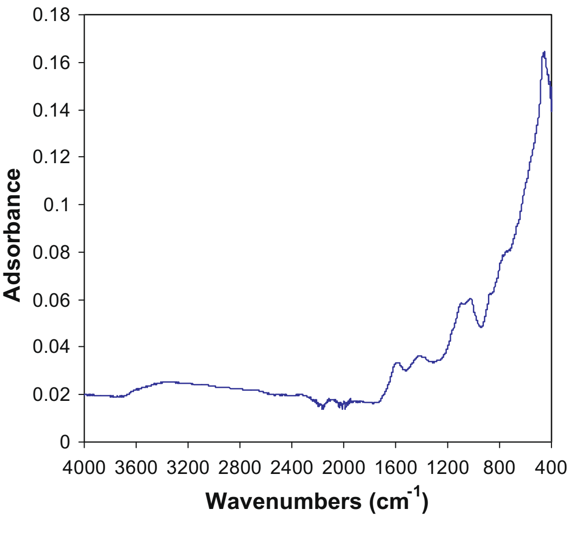

Fig. 6. FTIR spectra of paper sludge charcoal produced at 500 °C.

Properties of the produced charcoal are also important to determine its potential applications. Charcoal in this work was produced by pyrolysis of paper sludge to 500 °C at a heating rate of 10 °C/min. At this temperature 36% of the total dry paper sludge weight remained as charcoal. The produced sample was then subjected to proximate analysis, calorific value assessment and FTIR analysis. The charcoal sample was found to contain 32% fixed carbon, 12% volatile matter and 56% ash. Fig. 6 shows the FTIR spectra conducted on the produced charcoal from 400 to 4000 cm^{-1} using a Nicolet 6700 FTIR instrument with previous background subtraction. Results revealed an absorption band at 1590 cm^{-1}, which is associated with aromatic C=C vibrations, while the adsorption band detected at 1440 cm^{-1} correlates to overlapping C=C and C–H vibrations (Ishimaru et al., 2007). FTIR also showed bands at 1020 and 460 cm^{-1} corresponding to the inorganic fraction of the charcoal, most likely associated with silica and iron oxide, respectively.

The gross calorific value of the charcoal was measured with a bomb calorimeter and was determined to be 13.3 MJ/kg. This value corresponds very well with the empirical equation proposed by Cordero et al. (2001) for higher heating value of charcoals:

$$\mathrm{HHV(MJ/kg)} = 0.3543 \times \mathrm{FC\%} + 0.1708 \times \mathrm{VM\%}$$

where FC% and VM% are fixed carbon and volatile matter, respectively, both expressed in percentage of sludge weight.

4. Conclusions

- The bio-gas compounds produced during pyrolysis of paper sludge to 500 °C contained 24% of the paper sludge weight and had calorific value only sightly higher than the energy required to pyrolyse the dried paper sludge. However, when an industrial pyrolysis process is modelled, it is critical that the heat losses of the system, losses from the non-stoichiometric combustion conditions, and the excess energy required to remove the free moisture should also be accounted for and carefully considered.
- At 500 °C approximately 40% of the dry paper sludge weight was converted to liquid fraction with a composition consisting primarily of organic acids with linoleic acid being the most dominant bio-oil compound.
- Under the heating conditions examined in this work, 36% of the dry paper sludge weight at 500 °C is converted to charcoal. The charcoal contained large fraction of mineral matter (56%) with a calorific value of 13.3 MJ/kg.
- This study shows that pyrolysis of paper sludge may provide an alternative option for managing this waste and alleviate the need for landfilling. The energy potential of the produced biogas compounds can be utilised to recover the heat required for pyrolysis, hence reducing the requirement for external heat supply. The bio-oils and charcoal produced from paper sludge pyrolysis have the potential to provide marketable feedstock and sources of energy.

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